Zeolitic Imidazolate Framework-Derived Layered Double Hydroxides for Electrochemical Water Oxidation

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by

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CHAPTER-6

Conclusion and Future Perspectives

In this chapter, we have provided a concise review of the scientific contributions made in this thesis, as well as outcomes of our thesis works. This chapter provide essential insights for the development of efficient and cost-effective electrocatalysts derived from self-supported ZIF-67 for the electrochemical energy conversion technologies. In addition to this, we have also discussed the possible future perspective of ZIF-67 derived electrocatalysts.

6.1. Summary and Conclusion

OER is found as significant half-cell reaction in numerous electrochemical applications like water splitting and rechargeable metal-air batteries. Therefore, it is essential to develop efficient electrocatalysts with low overpotential and greater stability in order to enhance the sluggish kinetics of OER. Therefore, the goal of this thesis is to develop a relationship between crystal structure and electronic properties of the materials to get enhance OER activity. This thesis clearly focuses on development of layered double hydroxide materials. They possess remarkable OER activity due to tunable interlayer spacing and availability of abundance active sites as they have emerged as highly promising electrocatalysts for OER due to their unique 2D layered structures, easily customizable properties, and versatile chemical compositions. In our thesis work we have emphasized the advancements of LDH materials in enhancing OER performance through the regulation of their electronic structures. In addition to this, LDHs derived from ZIF-67, have characteristics like adjustable pore structures, high surface areas, unique morphologies, and dispersed metal active sites, which make them promising candidates for OER. This thesis discusses recent methodologies for improving the electrocatalytic activity of OER through modifications of ZIF-67-derived LDHs.

We have tried to achieve this goal through following way-

1) By doping various high valent transition metals (as we doped high valent transition metals V and Fe and then f-block element Ce and observed wide range of OER activity.)
2) By developing atomic level thickness of the as synthesized ultrathin nanosheets
3) By the formation of heterostructure which facilitates the charge transfer through interfaces
4) By varying the synthetic approach from hydrothermal technique to electrochemical

reconstruction of ZIF-67 into active catalysts

Table 6.1. Showing the OER activity of electrocatalysts designed in different of our thesis.

Sr. No.	**Catalysts**	**Precursor**	**Current density (mA cm^{-2})**	**Overpotential (mV)**	**Tafel slope (mV dec^{-1})**	**C_{dl} (mF cm^{-2})**	**Ref.**
1	$V_{0.2}$Co-LDH	ZIF-67	100	280	59	1.08	Chapter-2
2	$Fe_{0.4}$CoLDH@NF	ZIF-67	20	195	53	1.8	Chapter-3
3	FeCo-LDH-3	ZIF-67	50	180	48	47.87	Chapter-4
4	CeCo-2	ZIF-67	50	220	50	36.24	Chapter-5

6.2. Future scope and perspective

In our thesis work, we have made efforts to develop ZIF-67 based promising OER electrocatalysts. Still there are always possibility of improvement. Thus

i) ZIFs with new structures, morphologies, and properties can be designed and utilized as precatalysts for electrochemical reconstruction.

ii) As the majority of reported OER electrocatalysts have been tested in alkaline solutions. Therefore, the development of electrocatalysts based on ZIF-67 for a range of reaction conditions is crucial because in practical applications, water sources might be acidic, neutral, or complex, like seawater. To address the instability problem of ZIF-67-based electrocatalysts, development of efficient active electrocatalysts which are more pronounced in wide range of reaction medium.

iii) In our thesis, we have shown anodic reconstruction of self-supported ZIF-67 precatalyststs, this approach can be extended to other ZIFs precatalysts and investigated further to produce additional active catalysts for the electrochemical hydrogen evolution reaction. Furthermore, ZIF-derived active catalysts can be applied for overall electrochemical water splitting.

iv) Computational analysis should be widely employed to guide the rational design of ZIF-67-based electrocatalysts. Although some experimental characterization techniques can provide information about intermediates, theoretical computation offers in-depth insights to understand the catalytic mechanisms and support the experimental findings. Furthermore, computational predictions can aid in developing highly active electrocatalysts. Various computational analysis techniques should be performed in order to direct the rational synthesis of ZIF-67-based electrocatalysts. By leveraging computational tools, researchers can predict and optimize the electronic properties, structural stability, and catalytic performance of ZIF-67 materials. This approach enables the identification of key active sites, the evaluation of reaction mechanisms, and the prediction of the influence of various modifications on the catalytic activity. Consequently, computational analysis can significantly accelerate the development of highly efficient and cost-effective ZIF-67-based electrocatalysts for energy conversion and storage applications.

Despite the development of highly active ZIF-67 based electrocatalysts addressing numerous issues, still they are treated as highly desired candidates for the oxygen evolution reaction (OER) due to their special features. In the future, more facile and promising catalyst design strategies should be developed for the synthesis of novel ZIF-67 based electrocatalysts with enhanced electrocatalytic performance and long-term stability to meet the demands of practical water electrocatalysis applications.

List of publications

1. Maurya, P.; Vyas, V.; Singh A. N.; Indra, A. Iron(III) ion-assisted transformation of ZIF-67 to a self-supported Fe_xCo-layered double hydroxide for improved water oxidation. *Chem. Commun*. **2023**, 59, 7200-7203.

2. Maurya, P.; Ansari, T.; Indra, A. 4f-2p-3d orbital overlap in a metal-organic framework-derived CeO_2/CeCo-LDH heterostructure promotes water oxidation. *Chem. Commun*. **2023**, 59, 13359-13362.

3. Vyas, V.; Maurya, P.; Indra, A. Metal-organic framework-derived CoNx-nanoparticles on N-doped carbon for selective N-alkylation of aniline. *Chem. Sci.* **2023**, 14, 12339-12344.